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Carbon dioxide radical anion-based UV/$S_2O_8^{2-}$/HCOOH reductive process for carbon tetrachloride degradation in aqueous solution

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ABSTRACT

The reduction performance of carbon tetrachloride (CT) mediated by carbon dioxide radical anion ($CO_2^{\cdot-}$) was investigated in this study, and $CO_2^{\cdot-}$ was generated by the reaction of formic acid and sulfate radical produced in the UV/$S_2O_8^{2-}$ process. The effects of various factors including persulfate and formic acid concentrations, solution pH, and anions such as Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-} were evaluated. The experimental results showed that CT could be almost completely removed in 60 min with 1.50 mM persulfate and 2.25 mM formic acid. CT degradation efficiency was found to increase with increasing persulfate (0.75–4.50 mM) and formic acid (0.75–2.25 mM) concentrations. In the pH adjusted solutions (from pH 6–8), maximum CT degradation occurred at pH 6. Both Cl^- and NO_3^- (1–100 mM), as well as HCO_3^- at high concentrations (10 and 100 mM), adversely affected CT degradation performance. The addition of methyl viologen as $CO_2^{\cdot-}$ scavengers proved the presence of $CO_2^{\cdot-}$ in this UV/$S_2O_8^{2-}$/HCOOH process, and the dechlorination of CT was not complete as Cl^- release rate was 80.6% after 240 min.

1. Introduction

Chlorinated hydrocarbons (CHCs), such as carbon tetrachloride (CT), tetrachloroethene (PCE), trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) have been widely used for several decades as cleaning and degreasing solvents in chemical manufacturing. As a result of the extensive usage and improper operation during production, application, transportation, and storage, CHCs have become one of the most frequently detected organic pollutants in contaminated groundwater and at hazardous waste sites [1]. CT is one of the most commonly used CHCs and has been widely found in the National Priority List sites of USA [2]. As a priority toxic contaminant, CT is toxic to the liver, lungs, and kidneys and has been classified as a carcinogen by US Environmental Protection Agency [3] Therefore, the maximum contaminant level of CT in drinking water has been set at 0.005 mg L^{-1} in USA [4].

Persulfate anion ($S_2O_8^{2-}$) is a strong oxidant with a redox potential of 2.01 V, and has recently received considerable attention for contaminated groundwater and soil remediation. In most cases, various methods, including heat, ultraviolet irradiation, transition metals, hydrogen peroxide, alkaline, *etc.*, are applied to activate persulfate and generate the reactive species [5–11]. Upon activation, persulfate is capable of degrading a wide variety of contaminants, including chlorinated aliphatics and aromatics, fuel hydrocarbons, polycyclic aromatic hydrocarbons, and pesticides [12].

Thus far, the oxidative species, e.g., sulfate radical ($SO_4^{\cdot-}$, $E^0 \approx 2.6$ V) and hydroxyl radical ($^{\cdot}OH$, $E^0 = 2.7$ V), are generally understood as the key reactive species in persulfate activation system and to play a major role in organic contaminants degradation. In the thermally-activated persulfate system, it is proved that $SO_4^{\cdot-}$ is the predominant radical under acidic condition and $^{\cdot}OH$ is predominant under basic condition by means of chemical probe method or electron paramagnetic resonance technique [13,14]. In the UV-activated persulfate process, Liang et al. [15] demonstrated that $SO_4^{\cdot-}$ was the main radical responsible for phenol degradation at pH 3, while Xie et al. [16] found that the contributions of $^{\cdot}OH$ to 2-methylisoborneol and geosmin degradation were higher than $SO_4^{\cdot-}$ in the ultra-pure water at pH 7.

However, the reductive species, such as superoxide anion radical ($O_2^{\cdot-}$, $E^0 = -2.4$ V), are suspected to be important in persulfate chemistry as well [17,18]. Furman et al. [19] studied the mechanism of base activation of persulfate and confirmed the generation of $O_2^{\cdot-}$ during this process. Fang et al. [20] reported that $O_2^{\cdot-}$ was a critical factor in controlling the yield of $SO_4^{\cdot-}$ in the persulfate/magnetite nanoparticles system. Xu et al. [21,22] demonstrated that $SO_4^{\cdot-}$, $^{\cdot}OH$, and $O_2^{\cdot-}$ were all generated in the thermally-activated persulfate system, while $O_2^{\cdot-}$ appeared to be the predominant radical responsible for CT degradation, which was not expected to be susceptible to oxidation. Therefore, the reductive

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Table 1
Reactions involved in persulfate activation process with the addition of formic acid.

No	Reaction	Second order reaction rate constants ($M^{-1}\ s^{-1}$)	Reference
1	$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$	–	–
2	$2SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH$	6.5×10^7	[44]
3	$SO_4^{\cdot-} + HCO_2^- \rightarrow CO_2^{\cdot-} + SO_4^{2-} + H^+$	1.1×10^8	[23]
4	${}^{\cdot}OH + HCO_2^- \rightarrow CO_2^{\cdot-} + H_2O$	3.2×10^9	[23]
5	$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot}$	$(3.2 \pm 0.2) \times 10^8$	[33]
6	$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-}$	$(7.8 \pm 0.8) \times 10^9$	[33]
7	$Cl_2^{\cdot-} + Cl_2^{\cdot-} \rightarrow Cl_2 + 2Cl^-$	$(9.0 \pm 1.0) \times 10^8$	[33]
8	$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$	1.0×10^8	[33]
9	$Cl_2^{\cdot-} + HCOOH \rightarrow$ products	6.7×10^3 to 1.9×10^6	[34]
10	$SO_4^{\cdot-} + HCO_3^- \rightarrow CO_3^{\cdot-} + SO_4^{2-} + H^+$	$(2.8–9.1) \times 10^6$	[35]
11	$HCO_2^- + CO_3^{\cdot-} \rightarrow CO_2^{\cdot-} + HCO_3^-$	1.5×10^5	[36]
12	$HCO_3^- + CO_2^{\cdot-} \rightarrow HCO_2^- + CO_3^{\cdot-}$	2.0×10^3	[36]
13	$NO_3^- + SO_4^{\cdot-} \rightarrow SO_4^{2-} + NO_3^{\cdot}$	9.0×10^4	[38]
14	$HCO_2^- + NO_3^{\cdot} \rightarrow NO_3^- + CO_2^{\cdot-} + H^+$	$(3.3 \pm 1.0) \times 10^5$	[38]
15	$CO_2^{\cdot-} + MV^+ \rightarrow MV^{\cdot+} + CO_2$	$(6.3 \pm 0.7) \times 10^9$	[45]

mechanism in persulfate reaction could be applied in the degradation of refractory to oxidation contaminants, such as perchlorinated hydrocarbons.

Carbon dioxide radical anion ($CO_2^{\cdot-}$), a reductive species with a reduction potential of $E(CO_2/CO_2^{\cdot-}) = -2.0$ V, can be generated in persulfate activation process with the addition of formic acid or formate ions (reactions 1–4 in Table 1) [23]. Mora et al. [24] investigated thermal activation of persulfate and found that trichloroacetic acid was more efficiently decomposed in the presence of sodium formate via a reductive mechanism involving $CO_2^{\cdot-}$. Xu et al. [25] confirmed that CT could be effectively removed by the coupled thermally-activated $S_2O_8^{2-}$/HCOOH process, and CT degradation followed a zero order kinetic model. In addition, $CO_2^{\cdot-}$ was used in Hg(II) reduction by a combined application of the laser flash photolysis of persulfate and formic acid [26]. Our previous work revealed that the UV/$S_2O_8^{2-}$ process was shown to be effective in the degradation of 1,1,1-trichloroethane (TCA) and its volatile intermediates except CT [27]. Therefore, in this study, formic acid was added into the UV/$S_2O_8^{2-}$ process (UV/$S_2O_8^{2-}$/HCOOH) to enhance CT degradation, and the objective of this study was (1) to investigate the degradation performance of CT in the UV/$S_2O_8^{2-}$/HCOOH system, (2) to evaluate the effects of solution conditions such as persulfate and formic acid concentrations, solution pH, and anions on CT removal performance, and (3) to examine the presence of $CO_2^{\cdot-}$ in the system.

2. Materials and methods

2.1. Materials

The following reagents were purchased from Shanghai Jingchun Reagent Co., Ltd. (Shanghai, China) and used without further purification: formic acid (99.0%), sodium chloride (99.5%), sodium bicarbonate (99.5%), sodium nitrate (99.5%), sodium sulfate (99.5%), potassium iodide (99.0%) and methyl viologen dichloride (98%). Carbon tetrachloride (99.5%) and n-hexane (97%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Persulfate (98.0%) was purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water from Milli-Q water process (Classic DI, ELGA, Marlow, UK) was used for preparing aqueous solutions.

2.2. Experimental procedures

All of the photochemical experiments were conducted in a 1.0 L cylindrical glass reactor (an inner diameter of 7.0 cm and a height of 25 cm) with a quartz tube in the center of the reactor. The joint of the reactor and quartz tube was ground, and the sampling plot equipped with a ground glass stopper to avoid the loss of CT through volatilization. A low-pressure mercury vapor lamp (Guangdong, China, 10 W nameplate output at 254 nm) was placed in the quartz tube with a photon flux of 2.1×10^{-5} Einstein $cm^{-2}\ s^{-1}$ [28]. A magnetic stirrer was located at the base of the reactor to ensure the solution remained homogeneous. The reactor was filled with the reaction solution containing CT, persulfate, and formic acid and then the lamp was turned on for the initiation of experiment. The temperature was kept constant at 20 °C during all experiments with a cooling water jacket using a thermostat circulating water bath (SCIENTZ SDC-6, Zhejiang, China). The CT concentration in all tests was prepared in an aqueous solution and fixed at 0.15 mM. Aqueous samples were withdrawn at predetermined time intervals and analyzed immediately. The initial pH in all experiments was unadjusted except in the tests for investigating the influence of pH. All experiments were conducted in triplicate and the mean values reported.

2.3. Analytical methods

The concentration of CT was determined by a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with an electron capture detector, an autosampler (Agilent 7693), and a DB–VRX column (60-m length, 320-μm i.d., 1.4-μm thickness). The injection volume of sample was 1 μL with a split ratio of 20:1. The temperatures of the injector and detector were 240 and 260 °C, respectively, and the oven temperature was isothermal at 75 °C. The method detection limit (MDL) for CT is 5 μg L^{-1}. The volatile organic intermediates formed in CT degradation experiments were identified by the EPA SW-846 Method 5030B and 8260B using an automatic purge and trap (Tekmar Atomx, Mason, OH) coupled to a GC/MS (Agilent 7890/5975) and with the same DB-VRX column as before. The MDL for the volatile intermediates is 0.5 μg L^{-1}. The concentration of persulfate was quantified using a spectrophotometric method followed the procedures described by Liang et al. [29]. The pH was measured with a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland). The concentration of chloride ions was detected by ion chromatograph (Dionex ICS-I000, Sunnyvale, CA).

3. Results and discussion

3.1. Degradation efficiency of CT in the UV/$S_2O_8^{2-}$/HCOOH process

Fig. 1 shows the degradation of CT in the UV/$S_2O_8^{2-}$/HCOOH process. It can be seen that around 1.6% loss of CT due to the volatilization

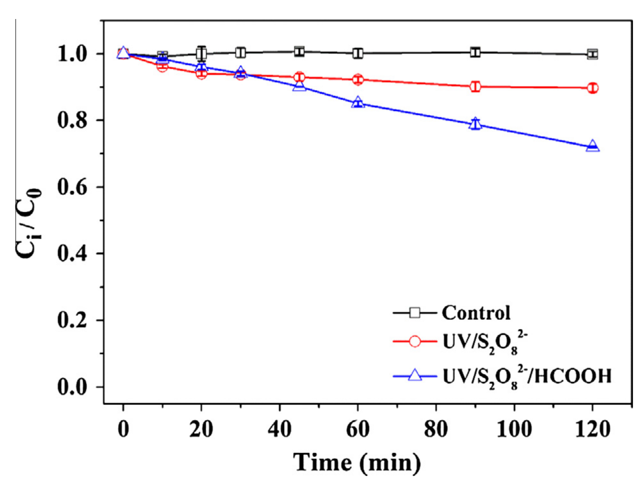

Fig. 1. CT degradation performance in the UV/$S_2O_8^{2-}$/HCOOH process (conditions: $[S_2O_8^{2-}]_0$ = 0.45 mM, [HCOOH] = 1.50 mM).